THE DETECTION OF ALPHA PRIME IN DUPLEX STAINLESS STEELS

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ABSTRACT

Duplex stainless steels are widely used by the oil and gas and chemical and process industries because of their combination of high strength and corrosion resistance. The alloys are usually used in the solution annealed condition and must be fast cooled from the annealing temperature to prevent the precipitation of third phases, such as sigma, chi, nitrides and alpha prime. Alpha prime precipitates in the temperature range 550 to 300°C. It forms less readily than sigma phase and other intermetallic precipitates and so is not normally found in commercially produced duplex alloys. However, poor cooling of duplex steels through this temperature range or repeated excursions in to this temperature range can result in its formation. Alpha prime dramatically reduces impact toughness and increases susceptibility to hydrogen induced stress corrosion cracking due to cathodic protection. However, corrosion resistance in chloride environments appears to be little affected by this phase. Alpha prime cannot be seen under optical microscopes, because of its very small size. This means that the combination of corrosion testing in ferric chloride solution, microstructural examination and impact testing, can be ineffective in detecting alpha prime precipitation, principally because of the low toughness acceptance level of 45 Joules at -46°C that is commonly specified. This paper describes a simple electrochemical reactivation test to detect alpha prime that can be used with both 22%Cr and 25% Cr alloys. The paper also presents some case studies where low toughness occurred but no third phases were visible in optical microsections. The test was used to confirm the presence of alpha prime and determine what should be done to correct the problem.

Key words: Duplex Stainless Steel; Third Phases; Impact Toughness; Hydrogen Embrittlement

INTRODUCTION

Duplex stainless steels are widely used by the oil and gas and chemical and process industries because of their combination of high strength and corrosion resistance, particularly to stress corrosion cracking (SCC). The most commonly used grades are 2205 (UNS S32205), 2507 (UNS S32750) and Z100 (UNS S32760). In order to get the best properties the alloys must be solution annealed at high temperature for sufficiently long to dissolve any third phases and to allow homogeneity in both the ferrite and austenite[1]. The alloys must then be transferred rapidly to a water quench tank so that the metal can be cooled sufficiently fast to prevent any third phases from forming. Figure 1 shows a typical CCT curve for superduplex stainless steel and it can be seen that sigma, chi and nitrides form at high temperatures, while alpha prime forms between 550 and 300°C. Although it requires a greater time at temperature for alpha prime to form, compared with sigma and chi, the cooling rate is slower at lower temperatures. This is a bigger problem for thick sections and Francis and Hebdon have discussed in detail the requirements in terms of quench tank volume to charge mass, as well as start and finish bath temperatures, to ensure a sufficiently rapid quench[2].

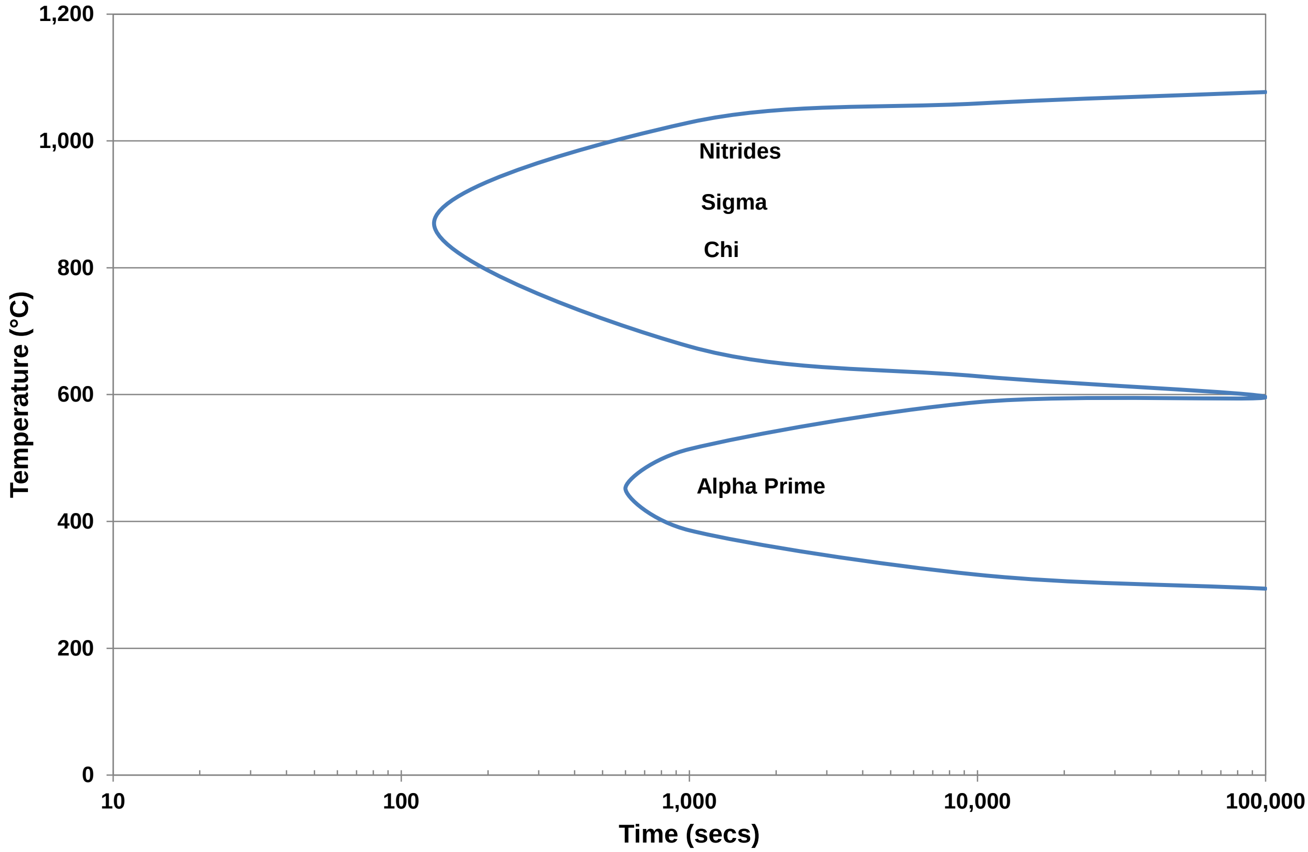

FIGURE 1 A typical CCT curve for superduplex stainless steel.

However, if the quench tank volume is insufficiently large, or the charge is removed from the tank soon after the surface temperature is below 300°C, it is possible for the centre of thick sections to spend sufficiently long at temperatures in the critical range for alpha prime to form.

One of the problems with alpha prime is its small size, which means it is not visible in optical microsections, even at X500 magnification. It can be seen by transmission electron microscopy, but this is a tricky and expensive operation. When a duplex alloy fails a qualification test and no cause is visible in the microstructure the presence of alpha prime may be suspected, but to date no specific test for it has been available.

ALPHA PRIME

Alpha prime is a chromium rich phase that is thought to form by spinodal decomposition, although a simple nucleation and growth mechanism at temperature cannot be excluded[1]. When formed by spinodal decomposition, alpha prime increases the hardness. However, some of the other properties degrade with small amounts of alpha prime, when a change in hardness is not easily detected. The effects of alpha prime on several properties are discussed below.

Impact Toughness

It is well known that alpha prime causes a large decrease in the Charpy impact toughness energy at low temperatures, as shown Figure 2.

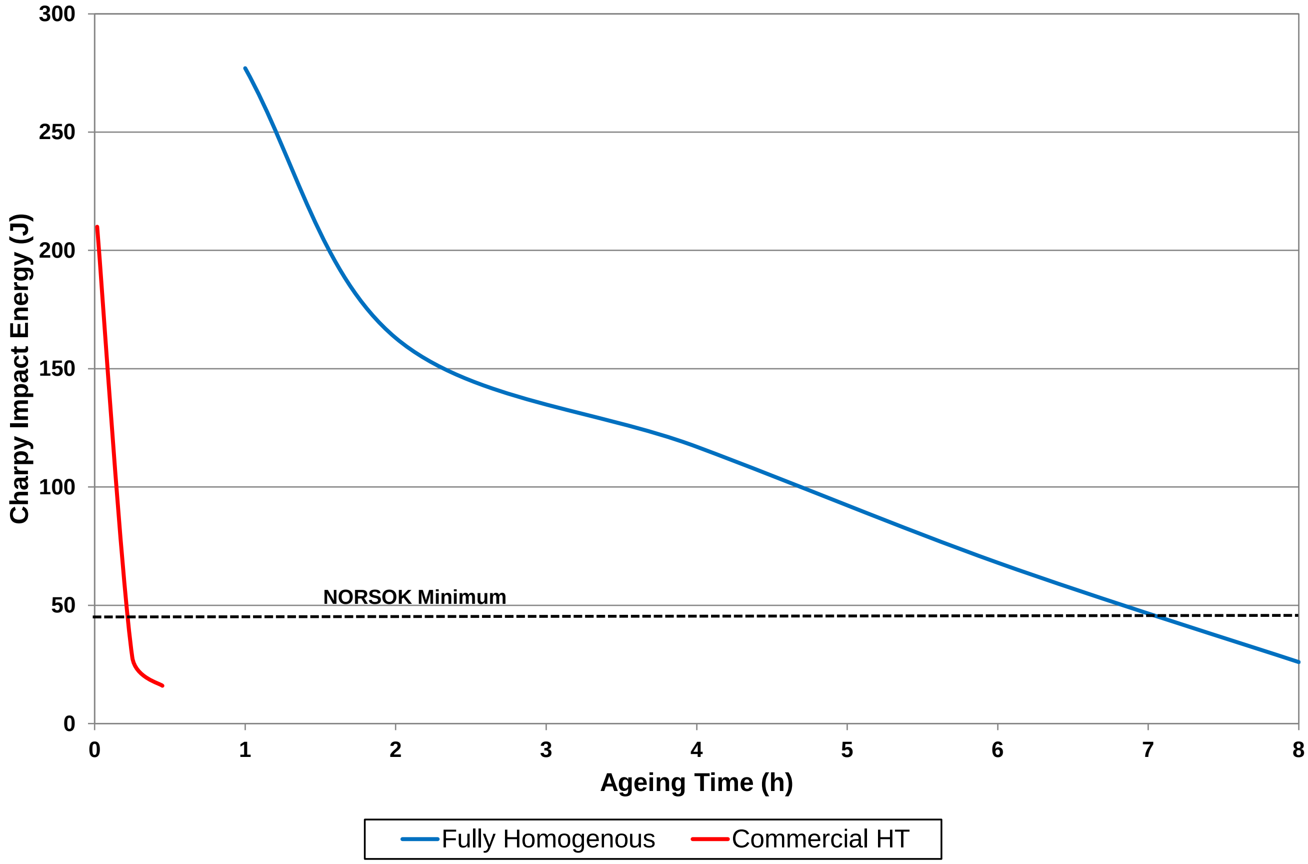

FIGURE 2 Charpy impact toughness energy at -46°C after ageing at 450°C.

The fully homogenous curve was derived in the authors' laboratory from Z100 12mm plate that was heat treated in the laboratory at 1120°C for 2 hours followed by water quenching. The Charpy impact toughness at -46°C was then determined for samples that had been aged for different times at 450°C. This is typical of curves from the literature, showing that it requires a long ageing time before significant toughness is lost. However, Bousquet et al did similar tests on a commercial heat of 2507 and showed that the toughness could decease significantly in under an hour at ageing temperatures[3]. This is because many commercial heats of duplex stainless steels are not fully homogenous, enabling more rapid precipitation of third phases under cooling that is not fast enough. A common requirement for impact toughness of duplex stainless steels is that in NORSOK M-630[(1) 4], which is an average of 45J at -46°C. It can be seen from Figure 2 that this value can be reached after just 10 minutes of ageing.

Corrosion

It is generally accepted that alpha prime has little effect on corrosion and the authors carried out critical

(1) Standards Norway, N-1326 Lysaker, Norway

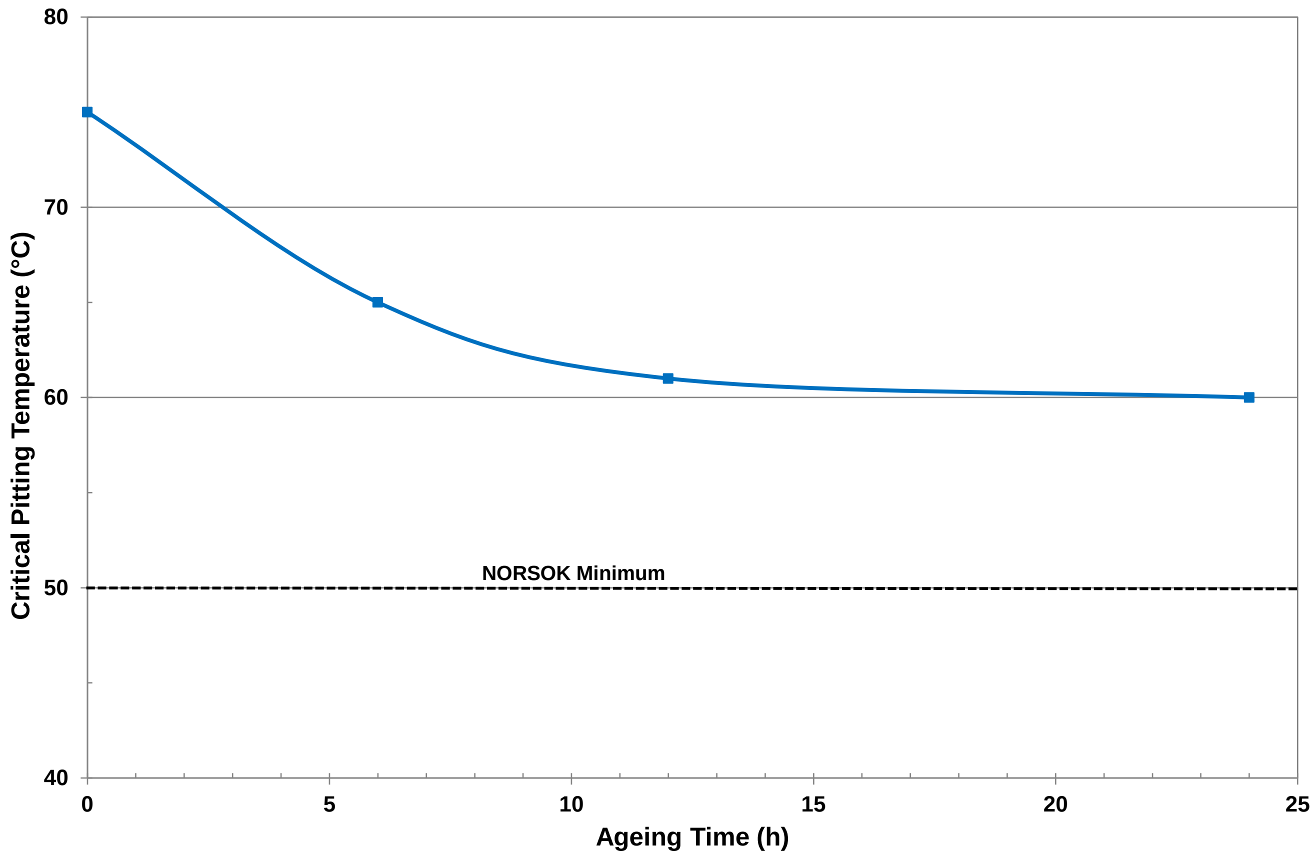

FIGURE 3 CPT to ASTM G48 E of alloy Z100 as a function of ageing time at 450°C.

pitting tests in ferric chloride solution to ASTM[(1)] G48 method E on alloy Z100 that had been aged for various times at 450°C.The results in Figure 3 show that the CPT only decreased significantly after 3 to 4 hours of ageing and even after 24 hours ageing, the CPT was high enough to pass the NORSOK M-630 criterion of 50°C. The reason that the alpha prime does not have a great effect on the CPT is because of its small size. The smaller the chromium-rich precipitate, the smaller is the chromium-depleted zone around it, with reduced corrosion resistance.

Hydrogen Embrittlement

It is well known that duplex stainless steels are susceptible to hydrogen embrittlement when used subsea with cathodic protection (CP), for example reference 5. There have been a number of service failures of duplex stainless steel due to hydrogen embrittlement and these led to the development of a guide to avoid embrittlement in service under CP[6]. However, this document takes no account of the possible presence of alpha prime and bases its design criteria solely on the austenite spacing.

Slow strain rate tests of alloy Z100 in 3.5% sodium chloride while polarized to -1.0V SCE showed a slight reduction in elongation for lightly cold worked material compared with testing in air (Figure 4)[5]. However, material aged at 475°C showed a large drop in elongation, demonstrating increased susceptibility to embrittlement. There have been a few failures in the North Sea of 25%Cr duplex stainless steel bolts that had been aged to increase their strength[5].

Summary

The results above show that alpha prime can precipitate in significant quantities in as little as 10

(1) ASTM International, West Conshohocken, PA, USA

minutes in the critical precipitation region. This is not detected by an ASTM G48 corrosion test, but it does affect impact toughness significantly. However, the low acceptance criterion in NORSK M-630 means that material with significant levels of alpha prime could be judged acceptable. This has risks not only for toughness, but also for susceptibility to hydrogen embrittlement.

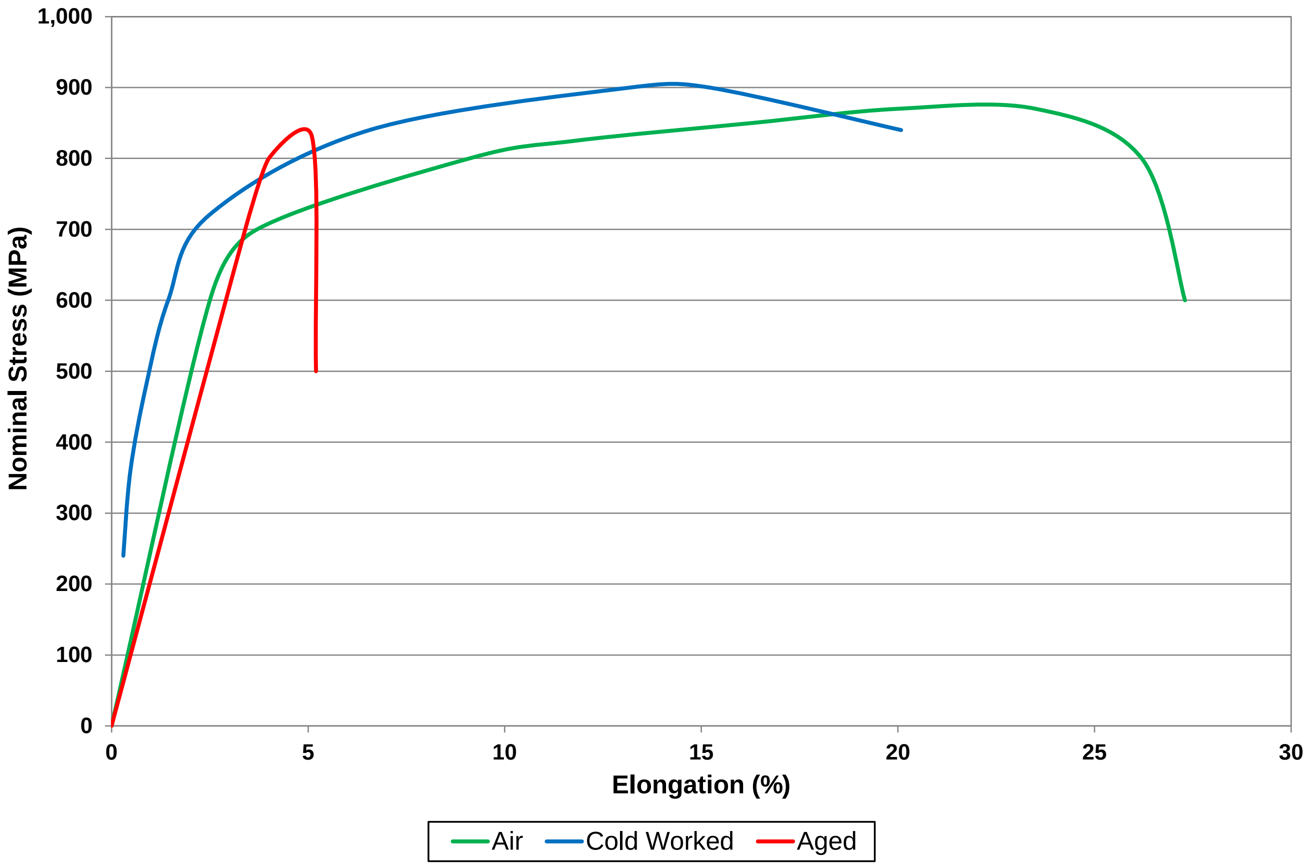

FIGURE 4 Slow strain rate tests of Z100 in 3.5% sodium chloride at -1.0V SCE in different conditions.

REACTIVATION TESTS

The susceptibility of 300 series austenitic stainless steels to sensitization can be assessed using a reactivation test, as in ASTM G108 [7]. Similar tests have been experimented with from time to time for the detection of undesirable precipitates in a range of alloys. Such tests are electrochemical and sweep the potential anodically until passivation occurs. The shape of the reactivation curve when the potential sweep is reversed then gives information about the presence, or otherwise, of precipitates. Such tests often use sulphuric acid with additions of another chemical that will aid in separating the reactivation reactions.

Hutchings devised a reactivation test for Z100, but it was necessary to use a much stronger solution, and the most suitable was 5M hydrochloric acid[8]. He experimented with different sweep parameters and identified the following as the best for alloy Z100:

Solution: 5M HCl
Potential Range: -800 to +200 to -800 mV SCE
Sweep Rate: 4mV/s
Surface Finish: 1200 grit

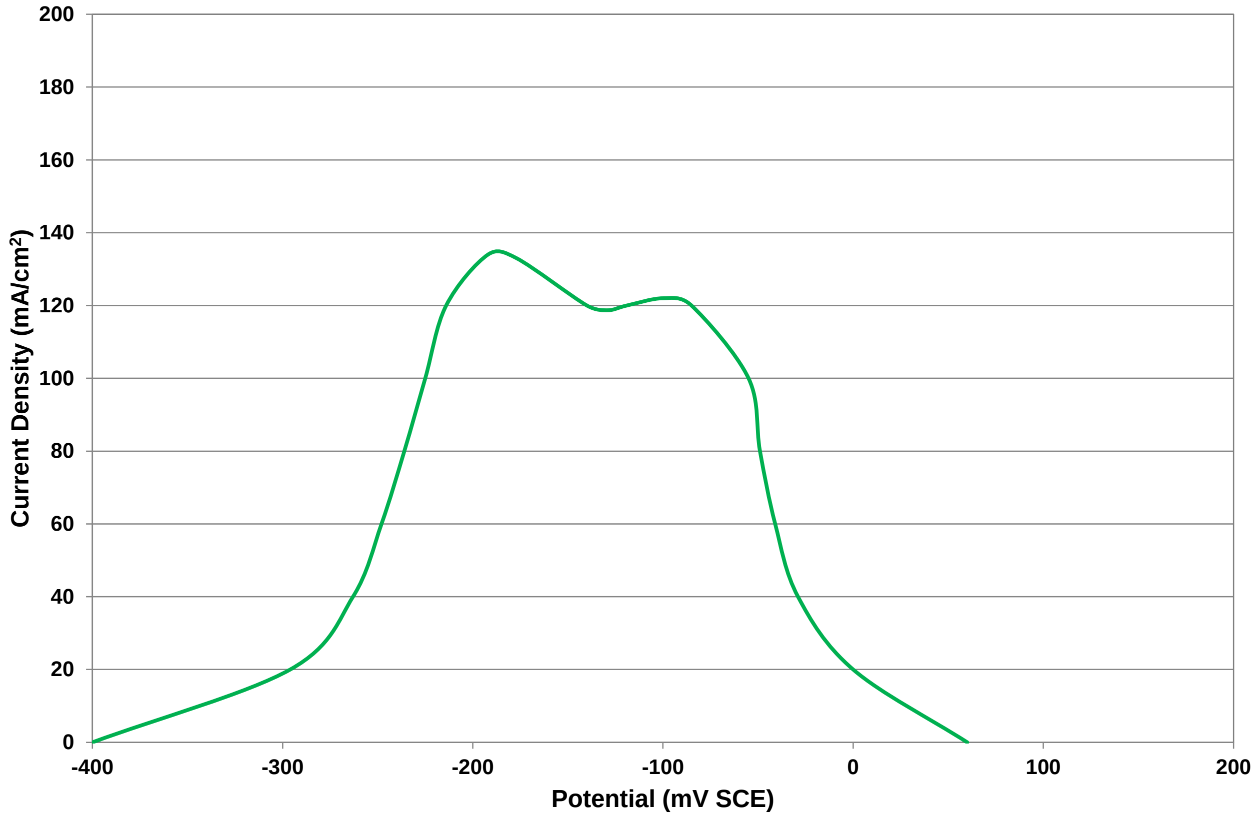

FIGURE 5 Reactivation curve for alloy Z100 containing no alpha prime.

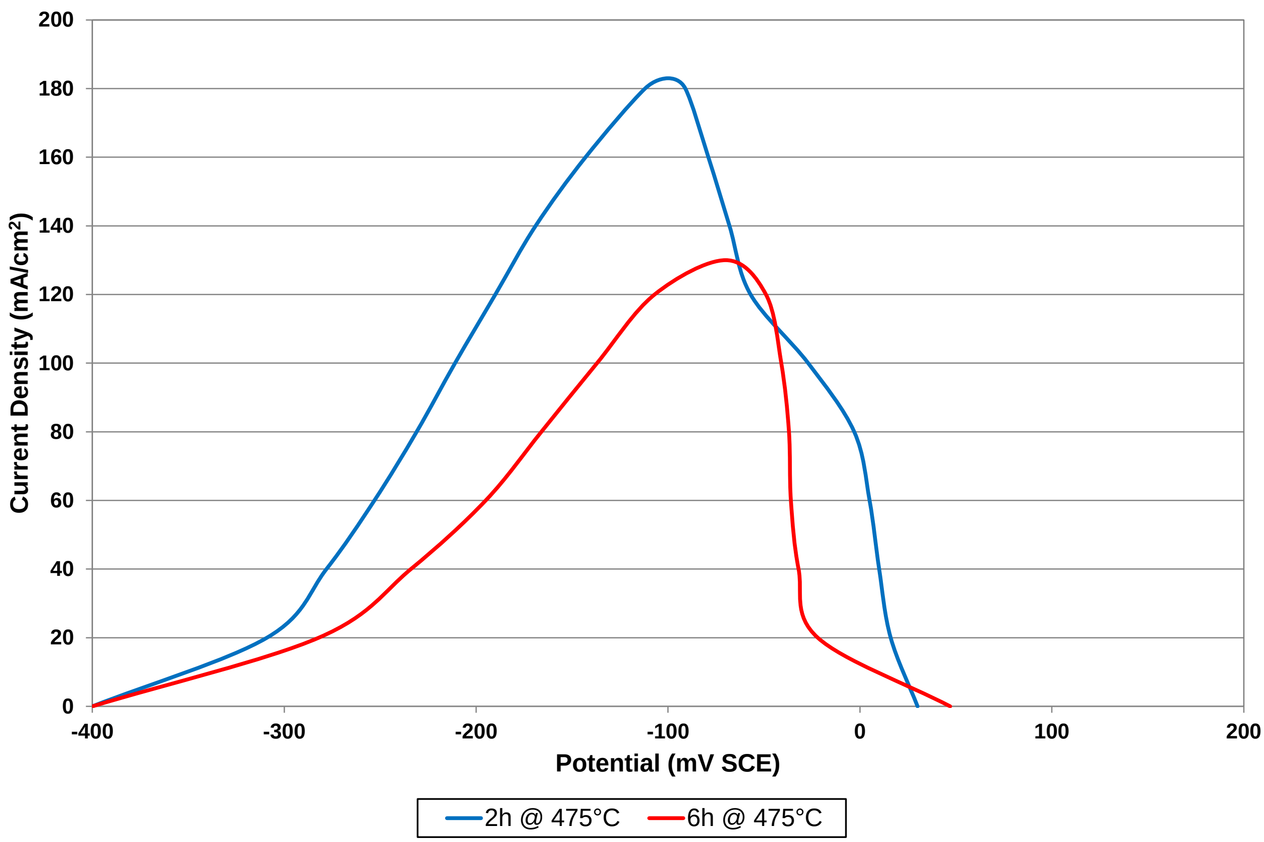

FIGURE 6 Reactivation curves for alloy Z100 with varying amounts of alpha prime.

The useful data is contained in the reverse sweep from +200 to -400 mV SCE. Figure 5 shows the reactivation curve for solution annealed material with no alpha prime. The curve clearly shows two separate peaks for austenite and ferrite. Figure 6 shows reactivation curves for material aged for two hours and six hours at 475°C, and classed as containing a little and a lot of alpha prime. Figure 6 shows that the ferrite peak gradually decreases as the alpha prime content increases. As the alpha prime precipitates in the ferrite, this change in the ferrite activation peak is not surprising. Another characteristic is the shoulder on the rising curve for material with a little alpha prime.

The authors have used the test with various different product forms (bar, plate, forgings etc) and the test works fine on all, with a surface finish of 1200 grit. The test does not work on welds, but it is very rare that there is a requirement to test welds for alpha prime, because they cool so quickly that alpha prime would be most unlikely to form. Because of the high current density in this test it is necessary to use a commercial lacquer to reduce the exposed area and prevent saturation of the potentiostat amplifier.

The authors have used the test with other 25%Cr duplex stainless steels and they generally follow the same trend as in Figures 5 and 6, but it is useful to do calibration curves first to see the shape of the curve with no alpha prime, and exactly what changes will occur as alpha prime content increases. The test has also been used with 2205 duplex stainless steel, but the test solution needed modification. In some quick tests it was found that 4M HCL gave two peaks, but not as distinct as in Figure 5. It is possible that reducing the concentration to 3.5M HCL might improve the resolution for 22%Cr duplex, but 3M HCl is too weak.

CASE HISTORIES

Case History 1

A well-known pump company was using superduplex stainless steel bar for shafts and they found that if they did all the machining in one go, the redistribution of interfacial stresses between the ferrite and austenite could cause the shaft to bend over a few hours. To overcome this, they tried partial stress relieving the bar at 350°C for two hours before machining. This was successful in stopping the bending, but the use of the electrochemical reactivation test showed the presence of a lot of alpha prime phase. Further testing was undertaken and it was found that partial stress relieving for two hours at 300 to 315°C also prevented the bending, but with only a small amount of alpha prime precipitation and an acceptable level of Charpy impact toughness.

Case History 2

Some large forgings in a proprietary 25% Cr duplex, similar to 2507, were giving low toughness, 32J at -30°C, but no third phases could be seen in the microstructure (Figure 7). When a piece of the forging was evaluated in the reactivation test, substantial amounts of alpha prime were found. It was recommended that the forging be re-annealed to dissolve the alpha prime and become homogenous before quenching faster to prevent it re-precipitating.

Case History 3

Some heavy section forgings (250mm) for valve bodies were produced in 2205 for use subsea. The Charpy impact toughness at -46°C was low (~20J) and did not meet the NORSOK requirements. Although the microstructure was free of third phases by optical microscopy, the authors detected significant quantities of alpha prime phase using the reactivation test in 4M HCl. Not only had the heat treatment time at temperature been for less than two hours, but the forgings had also been removed from the quench tank before the centre was below 300°C. The short heat treatment time dissolved the third phases but did not homogenize the composition, making precipitation on cooling easier.

Unfortunately the forgings had been machined before the impact toughness test results were available, so re-heat treatment was not considered feasible because of the risk of distortion.

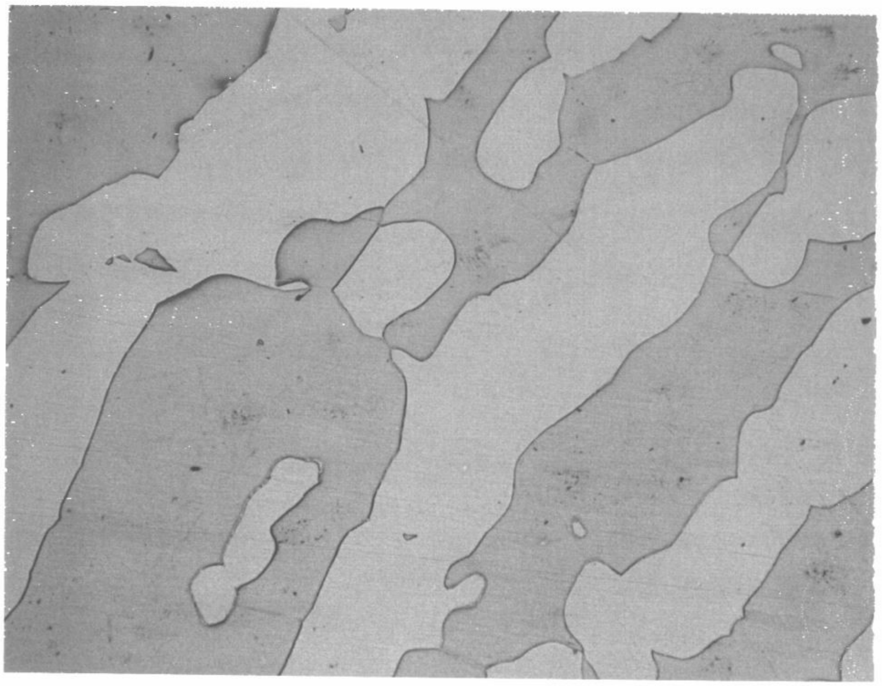

FIGURE 7 Microsection of 25%Cr forging showing no third phases at X500. (etched electrolytically in 10% oxalic acid followed by 40% KOH)

Because of time constraints, replacement valve bodies were ordered as ASTM A995 grade 4A castings. These were heat treated at 1120°C for 10 hours and were then quenched in a large, agitated and chilled water tank. Because the quenching was done at the end of the working day, the castings were left in the quench tank overnight. The castings were tested for alpha prime and no significant quantities were detected. The Charpy impact toughness energies at -46°C were high, with average values of ~100J at the ¼T position and ~80J at the ½T position. Castings have no directionality to their structure, so longitudinal and transverse does not apply. These results have nothing to do with differences between castings and forgings, but are due to getting the heat treatment right.

Case History 4

The authors examined some 25mm diameter bar to the UNS S32760 composition that had been manufactured in the Far East. The impact toughness at -46°C was 58J, when it would normally be expected to be 200J or more for a bar of this thickness. No third phases were visible in the microsection at X500 and so the bar was tested using the reactivation test, which showed large quantities of alpha prime to be present (Figure 8). The curve is offset slightly compared with Figure 6, but insufficient material was available for more extensive tests to ascertain the cause. It was recommended that the bar be not accepted and returned to the manufacturer for re-heat treatment.

Case History 5

Glenn; Add another???

CONCLUSIONS

1. Alpha prime can form rapidly in the temperature range 300 to 550°C in commercial heats of duplex stainless steel.

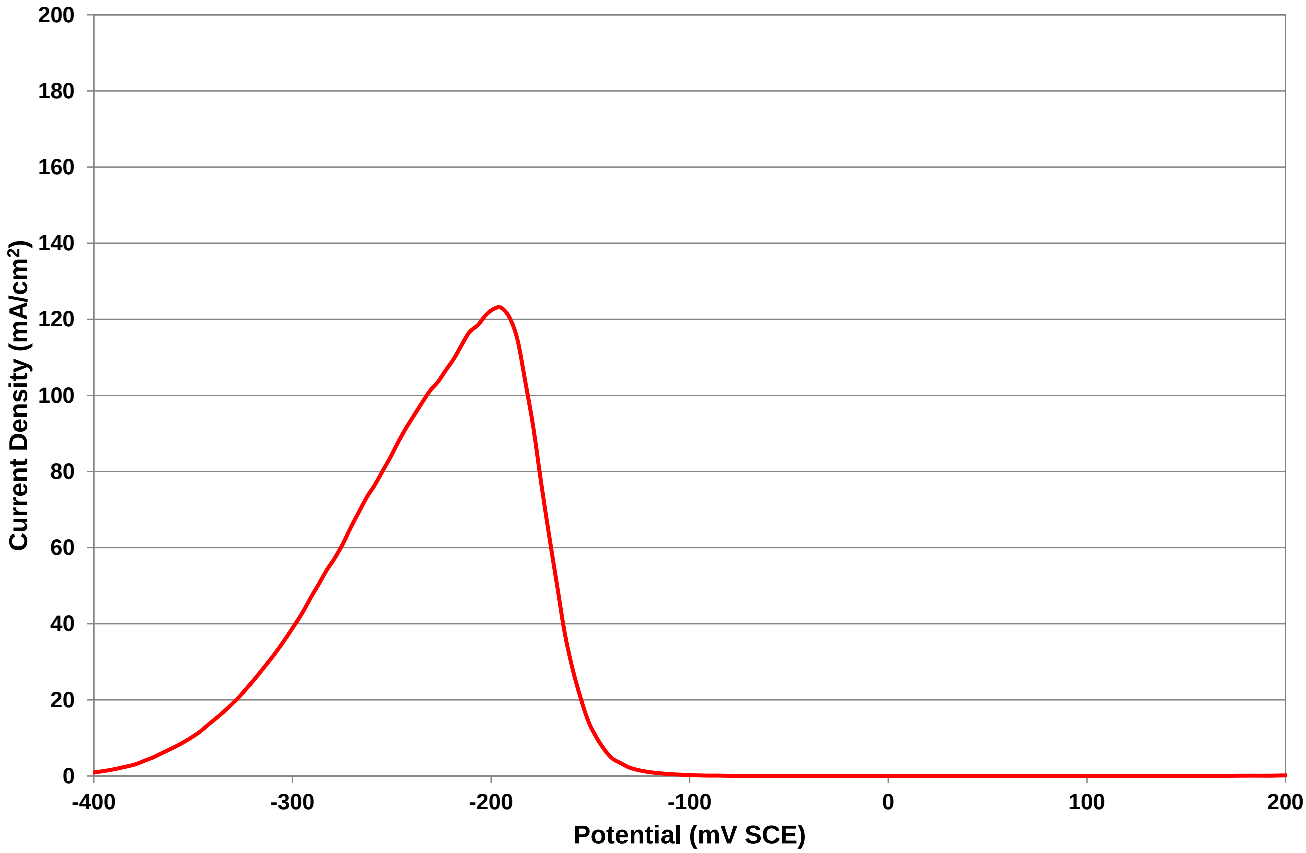

FIGURE 8 Reactivation curve in 5M HCl for a 25mm diameter superduplex bar.

2. The presence of alpha prime can cause a large reduction in Charpy impact toughness at low temperatures, and an increase in susceptibility to hydrogen embrittlement, but has little effect on corrosion resistance.
3. Alpha prime is not visible in optical micrographs at X500 magnification.
4. An electrochemical reactivation test has been devised that can show qualitatively the presence of alpha prime, using hydrochloric acid.
5. The test has been used in commercial applications to confirm the presence of alpha prime and suggest remedial measures.

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REFERENCES

1. J Charles, *Superduplex Stainless Steels: Structure and Properties*, Duplex Stainless Steels '91, Beaune, France, October 1991, les editions de physique, page 3.

2. R Francis and S Hebdon, *The Limiting Section Thickness for Duplex Stainless Steels*, Paper 3651, Corrosion 2014, San Antonio, TX, USA, March 2014, NACE International.

3. R. Bousquet, F. Roch, G. Gay and B. Mayonobe, Stainless Steel World, Dec 2002, page 21.

4. NORSOK M-630, Material Data Sheets for Piping, Edition 5, September 2010.

5. Dr R Francis, Dr G Byrne and G R Warburton, *Effects of Cathodic Protection on Duplex Stainless Steels in Seawater*, Corrosion, Vol. 53, No. 3, pp234-240 (1997).

6. Recommended Practice DNV-RP-F112, *Design of Duplex Stainless Steel Subsea Equipment Exposed to Cathodic Protection*, October 2008

7. ASTM G108, *Standard Test Method for Electrochemical Reactivation (EPR) for Detecting Sensitization of AISI 304 and 304L Stainless Steels*, ASTM International, West Conshohocken, PA, USA

8. D Hutchings, *Hydrogen Embrittlement of Duplex Stainless Steel*, PhD Thesis, University of Manchester, March 1994